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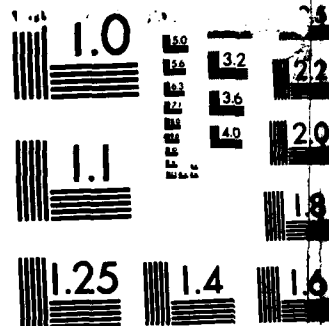
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TECHNICAL REPORT NO. 7

Non-Local Screening
in Metal Surfaces

by

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This paper makes a contribution towards the understanding of the electronic structure of metal surfaces. It demonstrates the importance of non-local screening of the Coulomb interaction effects between electrons.

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NON-LOCAL SCREENING IN METAL SURFACES

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ABSTRACT

We show that the effect of the non-uniform environment on the static screening of the Coulomb potential causes a major change in the calculated surface energy of simple metals.



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Density functional theory¹ (DFT) needs, for practical purposes, approximations to the exchange-correlation energy functional $E_{xc}[\rho_1(\mathbf{r})]$. Most common is the local density approximation (LDA) which is valid if the density $\rho_1(\mathbf{r})$ varies sufficiently slowly as a function of \mathbf{r} . It is not *a priori* clear whether this condition is satisfied in a metal surface.

As an alternative, we have recently (Ref. 2, hereafter called paper I) developed a variational theory for inhomogeneous Fermi systems. The theory has been shown to be accurate enough to provide, in the homogeneous limit, reasonable agreement with the known³ properties of the bulk system. But it can be evaluated without further assumptions on the slowness of the density variation. We have applied the theory to the calculation of electron densities, surface energies, and work functions of metal surfaces. We obtained surface energies of idealized jellium systems significantly higher than the ones predicted by density functional theory (DFT) in the local density approximation (LDA)¹. This letter reports on extensions of the calculations of I, and clarifies the origin of the larger surface energies.

The variational method for an inhomogeneous Fermi system starts with an explicit *ansatz* for the ground-state wave function

$$|\Psi_0\rangle = \exp\left\{\frac{1}{2} \sum_i u_1(\mathbf{r}_i) + \frac{1}{2} \sum_{i < j} u_2(\mathbf{r}_i, \mathbf{r}_j)\right\} |\Phi_0\rangle \quad (1)$$

$|\Phi_0\rangle$ is the Slater determinant of a set of single-particle orbitals $\phi_i(j) \equiv \phi_i(\mathbf{r}_j)\chi(i)$, ($i, j = 1, \dots, A$); the $\chi(i)$ are the spin-eigenfunctions.

The function $u_1(\mathbf{r})$ can be shown⁴ to cancel a set of point-reducible diagrams if an optimized single-particle basis is used, and $u_2(\mathbf{r}_i, \mathbf{r}_j)$ is determined by minimization of the

FHNC approximation for the ground-state energy,

$$\frac{\delta E}{\delta u_2} = \frac{\delta}{\delta u_2} \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = 0 \quad (2)$$

The single-particle wave functions can be generated by a one-body equation of the form

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (3)$$

where the effective one-body potential $U(\mathbf{r})$ is determined by functional minimization of the ground-state energy⁵.

$$\frac{\delta E[U]}{\delta U(\mathbf{r})} = 0. \quad (4)$$

This procedure is equivalent to the minimization of the FHNC ground-state energy with respect to the one-body density in the space of all densities that can be generated by a *local* single-particle potential. In that sense we have carried out the DFT program without the assumption of a slowly varying density.

The theoretical basis of I is the Fermi-hypernetted chain (FHNC//n) theory for inhomogeneous systems⁴. Using the FHNC//0 approximation, we have derived in I expressions for the correlation energy and equations determining the two-body correlations and the optimal single-particle potential. To review the main ingredients of the theory, we need a few definitions: The convolution products of two functions $A(\mathbf{r}_1, \mathbf{r}_2)$ and $B(\mathbf{r}_1, \mathbf{r}_2)$ is written as

$$[A * B](\mathbf{r}_1, \mathbf{r}_2) \equiv \int d^3 r_3 A(\mathbf{r}_1, \mathbf{r}_3) B(\mathbf{r}_3, \mathbf{r}_2). \quad (5)$$

$S_F(\mathbf{r}_1, \mathbf{r}_2)$ is the static form factor of the model system described by $|\Phi_0\rangle$, inverses like

$S_F^{-1}(\mathbf{r}_1, \mathbf{r}_2)$ are understood in the sense of the convolution product (5), and

$$H_1 \equiv -\frac{\hbar^2}{2m} \frac{1}{\sqrt{\rho_1(\mathbf{r})}} \nabla \rho_1(\mathbf{r}) \cdot \nabla \frac{1}{\sqrt{\rho_1(\mathbf{r})}} \quad (6)$$

The Euler-Lagrange equation for the two-body correlations can be formulated as an equation for the inverse of the static structure function $S(\mathbf{r}_1, \mathbf{r}_2)$ (c.f. Eq. (B.2) of I):

$$[S^{-1} * H_1 * S^{-1}](\mathbf{r}_1, \mathbf{r}_2) = 2\tilde{V}_{p-h}(\mathbf{r}_1, \mathbf{r}_2) + [S_F^{-1} * H_1 * S_F^{-1}](\mathbf{r}_1, \mathbf{r}_2) \quad (7)$$

$\tilde{V}_{p-h}(\mathbf{r}_1, \mathbf{r}_2)$ is the particle-hole interaction. It can be expressed in terms of the Coulomb potential $v_c(|\mathbf{r}_1 - \mathbf{r}_2|)$ and the diagrammatic quantities defined in the FHNC theory. Its precise analytic form may be found in I. For our present purposes it is sufficient to write $\tilde{V}_{p-h}(\mathbf{r}_1, \mathbf{r}_2)$ in the form

$$\tilde{V}_{p-h}(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{\rho_1(\mathbf{r}_1)} v_c(|\mathbf{r}_1 - \mathbf{r}_2|) [1 - G(\mathbf{r}_1, \mathbf{r}_2)] \sqrt{\rho_1(\mathbf{r}_2)}. \quad (8)$$

The form (8) introduces the static screening factor⁶ $1 - G(\mathbf{r}_1, \mathbf{r}_2)$. We find it for inhomogeneous systems most convenient to formulate screening in configuration space.

The total energy in the FHNC approximation used in I has the form

$$E = T_F + E_{es} + E_x + E_c \equiv E_{HF} + E_c, \quad (9)$$

where T_F is the kinetic energy of the model system, E_{es} is the electrostatic energy, and E_x is the exchange energy, all calculated in the single-particle basis $\{\phi_i\}$. E_c is the correlation energy. We have expressed the correlation energy as

$$E_c = \Delta E_{pot} + \Delta T_{JF} + E_{RPA} \equiv E_{RPA} + \Delta E_c \quad (10)$$

where

$$E_{RPA} = -\frac{1}{4} \int d^3r [S_F * (S^{-1} - S_F^{-1}) * H_1 * (S^{-1} - S_F^{-1})](\mathbf{r}, \mathbf{r}). \quad (11)$$

The analytic forms for ΔE_{pot} and ΔT_{JF} are given in I; they are irrelevant for our present purpose. E_{RPA} is the RPA contribution to the correlation energy calculated with the *screened* particle-hole interaction (8). Setting $G(\mathbf{r}_1, \mathbf{r}_2) = 0$ in Eq. (8) and ignoring ΔE_c corresponds to a "collective" RPA, which is equivalent to the ordinary RPA if the particle-hole spectrum is replaced by an effective collective mode⁷. This "collective" approximation reproduces, in the bulk system, the RPA for the correlation energy and the static structure function within a few percent⁸. In the RPA, Eq. (7) determines the static structure function $S(\mathbf{r}_1, \mathbf{r}_2)$, which is then used to calculate the correlation energy via Eq. (11).

In I, we have chosen to consider jellium slabs which are translationally invariant in the $x - y$ plane and symmetric about $z = 0$. We have solved the coupled FHNC/Euler-Lagrange/Hartree-Fock equations for values of r_s corresponding to the metals *Al*, *Pb*, *Mg*, *Li*, *Na*, and *K* and for slab dimensions $d = 8, 10, 12$, and $14 a_0 r_s$. (a_0 is the Bohr radius). From the ground state energy as a function of the particle number n we can obtain by a linear fit $2\sigma_u = E(n) - e_\infty n$ both a surface energy σ_u and a bulk energy per particle, e_∞ . A corresponding construction can be made independently for each of the energy contributions spelled out in Eq. (10).

Table 1 shows, for the above-mentioned materials, the decomposition of the total jellium surface energy σ_u into contributions originating from the Hartree-Fock energy contribution E_{HF} , (σ_{HF}), the RPA energy E_{RPA} , (σ_{RPA}), and the correlation energy correction

$\Delta E_c(\sigma_c)$. We see that the Hartree-Fock and the RPA contributions dominate σ_c by an order of magnitude. We shall therefore ignore σ_c in the following discussion.

The total surface energies shown in Table 1 are throughout higher than those obtained by Lang and Kohn¹. In order to understand the difference, we have performed an array of test-calculations using different single-particle wave functions and energy approximations (Fig. 1):

- (i) In order to test the dependence of the FHNC approximation for the surface energy on the single-particle wave functions, we have performed optimized FHNC calculations with single-particle wave functions generated by a local density- functional calculation in the sense of Lang and Kohn from the bulk FHNC equation of state. We found that the surface energies from these calculations agree, within a few percent, with the ones obtained in I.
- (ii) We have obtained a density-dependent static screening function $G_{bulk}(\rho, |\mathbf{r}_1 - \mathbf{r}_2|)$ from an FHNC calculation for the bulk electron gas, and used it in local density approximation

$$G(\mathbf{r}_1, \mathbf{r}_2) \approx G_{bulk}(\rho(\mathbf{r}_{cm}), |\mathbf{r}_1 - \mathbf{r}_2|), \quad (12)$$

to solve Eq. (7) and to calculate the RPA energy (11) (LDS approximation). $\mathbf{r}_{cm} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the center of mass coordinate of the two particles. To guarantee the agreement between the kinetic, Coulomb, and exchange energies, we have used the single-particle orbitals obtained in (i). We found that the surface energies obtained in this way are significantly lower than the FHNC results of I, but in good agreement with the Lang-Kohn results.

- (iii) We have calculated, in our geometry, the surface energy by the Lang-Kohn procedure, using the bulk FHNC and RPA energy per particle. We found surface energies in agreement

with the Lang-Kohn results within a few percent.

(iv) We have performed a variational RPA calculation, i.e. solved equation (7) with $G(\mathbf{r}_1, \mathbf{r}_2) = 0$ and obtained the correlation energy from Eq. (11). We found that the surface energies agree within a few percent with the LDS calculation (ii) and the LDA (iii).

The agreement between the surface energy obtained in the LDA from different equations of state, as described in (iii) shows that the surface energy does not depend sensitively on the equation of state. The agreement described in (i) similarly shows that the correlation contribution to the surface energy is insensitive to the details of the one-body density.

The excellent agreement between the surface energy obtained in the RPA (procedure (iv)) and the LDA is unexpected and at present unexplored. Our result differs somewhat from the conclusions drawn from studies of surface-plasmon contributions^{9,10} to the surface energy. The agreement deserves further investigation, but it is not the main point of our study.

Calculation (ii) finally traces the source of the difference between the full FHNC calculation of I. and the LDA: This difference is caused, apart from the small correction σ_c , by the use of different static screening functions $G(\mathbf{r}_1, \mathbf{r}_2)$. We conclude that this function (and the related particle-hole interaction $\tilde{V}_{p-h}(\mathbf{r}_1, \mathbf{r}_2)$) is poorly described by the local density approximation (12). The difference between the static screening function in the LDS and in the inhomogeneous FHNC is not very large: We show in Fig. 2, for Na , the local screening function obtained from the inhomogeneous FHNC, parallel and perpendicular to the surface, and the LDA (12) for the same function, for different values

of the center of mass coordinate z_{cm} . The three sets of curves correspond to the center of mass located at $0.41a_0r_s$ outside the jellium edge, on the jellium edge, and $0.81a_0r_s$ inside the jellium edge. The last value corresponds to the maximum of the first Friedel oscillation. The basic observation is that $G(r_1, r_2)$, obtained in the inhomogeneous FHNC, is closer to its form in the bulk as the LDA. The rather small difference in the local screening function induces, however, a significant change of the surface energy.

We come, therefore, to the main conclusion of this work: *The local density approximation for the particle-hole interaction is inadequate in metal surfaces.* While we have confidence in the qualitative significance of our observation we are, due to the delicacy of the effect, presently not prepared to estimate the quantitative accuracy of our results. The FHNC//0 approximation used here is the *minumum* level at which the effect can be studied, but it is improvable. It is also not clear whether the assumption of *local* and *static* screening is sufficient.

Our conclusion that the LDA for the particle-hole interaction is inadequate can be made quite plausible considering the surface of a *self-bound* system like liquid ^4He or ^3He . A homogeneous phase of these systems does not exist below the density where the velocity of sound vanishes. Any LDA for the particle-hole interaction that one might invent must therefore predict an instability against density fluctuations. Nevertheless, the particle-hole interaction of two particles in a surface should never predict an instability, it must therefore deviate significantly from any LDA. We have obviously seen that this effect, while not mandatory for stability, is also significant in the electron liquid surface.

We have identified the point where the LDS fails for metal surfaces, and what needs to

be done to improve upon the LDA in these systems. Simplifications of the FHNC theory may now be found *a posteriori* that would allow the same calculational accuracy with simpler computational tools.

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r_s	<i>Metal</i>	σ_{HF}	σ_{RPA}	σ_c	σ_u
2.07	Al	-1273	994	57	-222
2.30	Pb	-674	812	43	181
2.66	Mg	-215	561	37	383
3.28	Li	5	328	27	360
3.99	Na	40	200	21	261
4.96	K	35	116	8	159

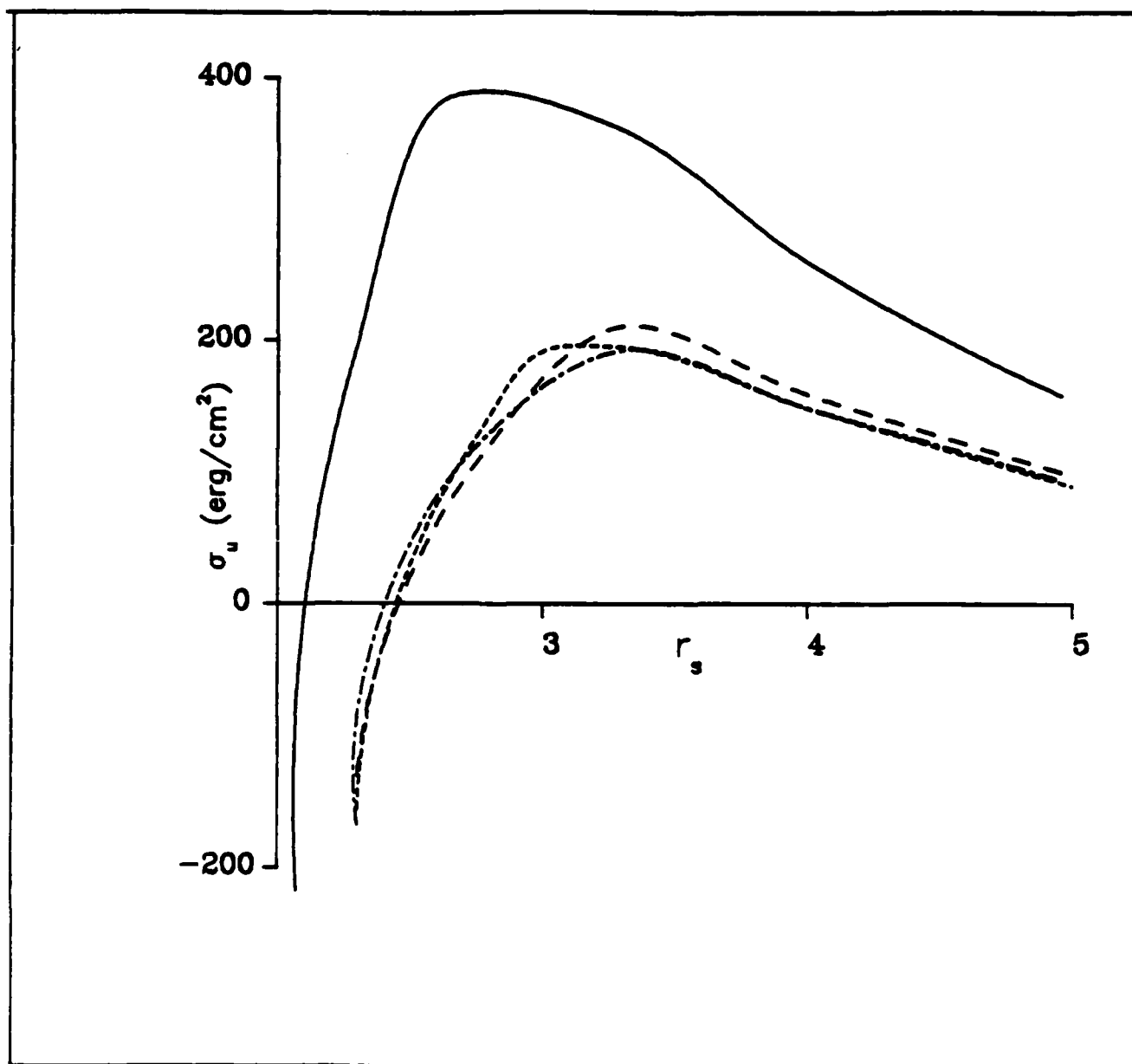
TABLE 1

Decomposition of the total surface energy σ_u into its contribution from the Hartree-Fock energy σ_{HF} , the RPA part of the total energy σ_{RPA} , and the correction σ_c .

Figure Captions

Fig. 1 The surface energy of jellium slabs obtained in the different procedures described in the text is shown as a function of r_s : The FHNC result of I (solid line), the RPA with the LDA (12) for the local screening function (long-dashed line), the Lang-Kohn result (dash-dotted line), and the variational RPA (short-dashed line).

Fig. 2 The local screening function $G(\mathbf{r}_1, \mathbf{r}_2)$ is shown, at different values of the center of mass-coordinate z_{cm} relative to the jellium edge, parallel (solid line) and perpendicular (dashed line) to the surface. Also shown is the local density approximation for the same function (circles).



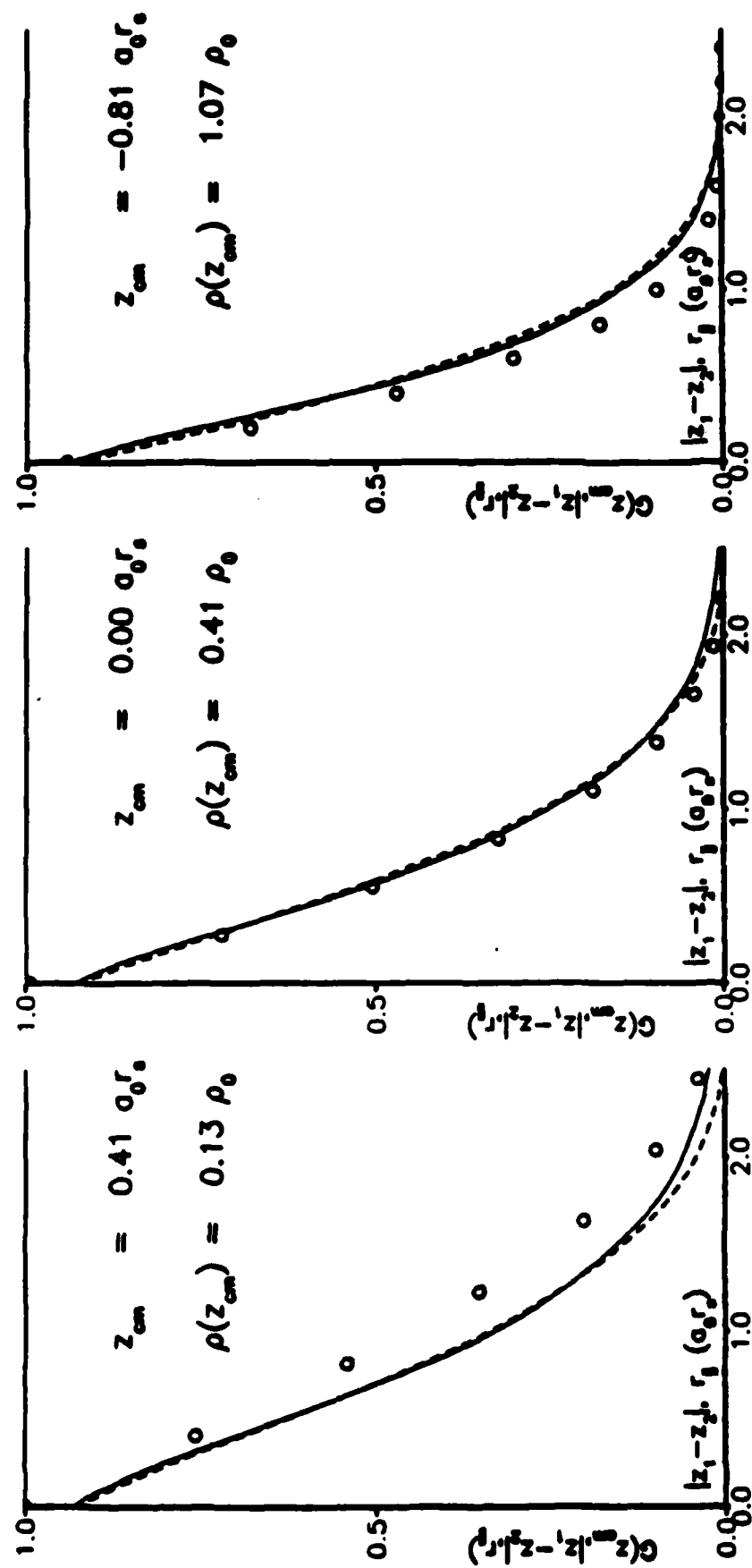


Fig. 2

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